

Development of Industrial Automotive Paint with Natural Raw Material Castor Oil as a Substitute of Polymeric Plasticizer

Shambhu Sharan Kumar

Abstract— Polymeric materials from natural resources have engrossed a set of developmental interests in recent years. The development of low priced automotive paints by the use of castor seed oil which has been introduced as a substitute of polymeric plasticizer materials focusing at this time to the polymer and paint industries due to the massive world wide availability, embedded biodegradability, low cost, and outstanding environmental characteristics (i.e., low toxicity toward human beings). The advantages of these outstanding natural characteristics are now being taken in the fields of research and development. Oil derived polymeric materials and composites are being utilized in many applications including paints, surface coatings, adhesives and nanocomposites. The endeavor of this research paper is likely to provide a basic enlightenment on the castor seed oil applications in polymeric activities with reference to their recent developments. Particular emphasis has been placed on the study and applications of drying oils in almost all low priced decorative and protective surface coatings. For the purpose of extraction of the oil, simple distillation method was used. Paint formulations i.e., the theoretical formulation, milling with calculated constituents to get mill-base, grinding and dispersion of pigment particles, stabilization, let-down and make-up processes were carried out within the laboratory conditions. Different paints were formulated by incorporating the base pigment rutile TiO_2 , alkyd resin alongwith other constituents as determined. The compatibility, viscosity, opacity, gloss, adhesion, flexibility and other quality control tests of castor seed oil plasticized automotive paints were carried out as per ASTM/BIS test methods and compared with the testing's standard of the Berger Paints Limited. The results were found as specific gravity: 0.95 ± 0.02 , refractive index @ 28°C : (1.79 ± 0.01), viscosity @ 28°C : (0.425 ± 0.12), pH: (5.800 ± 0.00), flash point: ($256.000 \pm 1.20^\circ\text{C}$), adhesion: 100%, gloss: 95-99%, 650 hours passed in salt spray test and 600 hours passed in weathering resistance test; all parameters were within the range of automotive paint applications and quality specifications. Castor-seed-oil has been appraised as an effective plasticizer and film-former in automotive paint formulations. The humidity content of the castor seeds was low, therefore, has been introduced as a material of good quality for the further use in other glossy automotive paint formulations.

Index Terms- Alkyd resin, castor-seed-oil, automotive paint, pigment, plasticizers.

I. INTRODUCTION

Paints normally are pigmented resin alongwith compatible solvents and additives, which after application to a substrate surface, form solid and protective films after drying as well as curing. In the ancient time, paints were prepared from

egg-shells, insects, plant-extracts, animals-fats, minerals, grinded rocks as pigment, natural resins and water as a common solvent had been improved gradually by applying modern technology to get better quality of paints and durable surface coatings [1,2,3]. Detailed study has shown that modern paints are being prepared to comprise shape (amorphous to crystalline), size (from micron to nano), structure, dispersion stability, film-uniformity, good looks, required quality and durability to both exterior and interior finishes in automotive vehicles by incorporation of suitable plasticizers with other essential ingredients [2,3,7,9]. The surface coating technology for automobiles as well as for different end-users have been more sophisticated and tailored, based on optimum preparation of blends of resins, compatible solvents, pigments, fillers, additives, curing agents and extenders for the purpose of better protection and to inhibit corrosion, cracks, erosion, resistance to heat, fire and cosmic rays, and designed to withstand in other adverse weathering and environmental conditions [1,2,10,21].

Modern Environmental Regulation Act has been advising for a long to chemical and paint industries to reduce solvent-emission by their paint-products to avoid air pollutions [9,10, 20]. This is because of the enormous use of conventional organic solvents in paint formulations that evaporate into the air during the manufacturing & drying processes by releasing the green house gases, cause global-warming and are harmful to living beings [9,16,22]. Therefore, castor oil, one of the drying vegetable oils is derived from the castor- seed-oil plants (*ricinus communis*). It is one of the most broadly used film-forming oil with applications in lubricants, decorative film and surface coatings. The castor-seed plants are widely available throughout the tropical regions of India, Africa and middle areas of the world, where these are cultivated as patterned blossoming plants [3, 15, 19]. The spring crop which is greenish to reddish-purple shells when matured contains like the large oval shiny bean-seeds [4,5,6]. The seed oil is colorless to light yellow with mild odor and is of their medicinal use in the treatment of constipation, wounds, skin diseases etc [3,5,7]. The presence of ricinoleic acid (a mono-saturated compound) with 18 carbon fatty acid having hydroxyl group on the 12th carbon which makes derivatives of other compounds like alkyd resins. It is one of the drying oils that achieved cross-linking on exposure to air to form a solid dry film; the property that make it unique constituent in automotive paint preparations [6, 8, 11].

Plasticizers are inert polymeric materials with high boiling point and functions by implanting themselves between the paint constituents to improve their cross-linking reactions [10,11,13]. They are dispersants or additives that could

Manuscript received December 13, 2015.

Shambhu Sharan Kumar, Assistant Professor, Chemistry Dept., Birla Institute of Technology, Mesra, Ranchi, Extension Centre, Allahabad- 211 010, India, Mobile No. +91 9451731437.

Development of Industrial Automotive Paint with Natural Raw Material Castor Oil as a Substitute of Polymeric Plasticizer

increase the plasticity, flexibility, compatibility, washability and durability of automotive paints or glossy paints [12,13,21,22]. Observations have shown that plasticizers had been used to improve the strength of glass-fiber reinforced plastic motor cases, concrete clays and related products [20,21,22]. An un-plasticized surface coatings result into loss of flexibility, embrittlement and cracking within a framed period of time [15,16,20,31]. Severe damages had been observed as it concerns maximum average loss in strength of motor cases without plasticizers than those with plasticizers [16,18,33]. Several medical reports had also shown that plasticizers are also used to improve hormone-like and estrogenic activities in the human body [17,19,35,37]. Research people had compared other drying oils with this oil and found that castor seed oil is good for most chemical or medicinal products like as an ingredient in the production of cosmetics and coatings etc [16,28,37].

At the same time as a part of my contribution to the improvement in paint properties, cost effectiveness, and health standard, minimization of organic solvent emission as the dangerous gases by paints and to improve the quality of industrial automotive top coats were explored. The extraction and application of castor-seed-oil as a plasticizer in automotive paints may be an alternative in place of imported costly linseed oil for automotive and glossy paint manufacturing [19,40,41].

II. MATERIALS AND METHODS

Essential equipments were used: a stopwatch, leveling cup, viscometer cup, refractometer, Hegman-gauge, soxhlet extraction set, water-bath, thermometer, heating arrangement, stirrer, mild steel panels and paint applicator etc, whereas the materials were taken: rutile titanium dioxide pigment, xylene, white spirit, nitrocellulose, alkyd resin, and castor-oil seeds etc.

Castor-oil seeds were taken from local market. Their hard shells were carefully separated and the obtained soft seed-extracts were weighed, heated to remove the moisture contents and weighed again. The extraction of the oil was carried out at 210-250⁰C using soxhlet-extractor and petroleum ether as a solvent. The test-analysis of oil sample was carried out to ensure its suitability in automotive paint preparation following the ASTM/BIS test methods. The viscosity measurement was carried out with the help of Ford-cup-B-4 at room temperature using a stop watch to monitor the time of flow resistance of the castor oil. Specific-gravity at the pressure of 1 atmosphere was calculated and the value was reported using the formula:

$$\text{Specific gravity (SG)} = \frac{\text{Weight of oil sample}}{\text{Weight of water}}$$

The refractive-index was recorded using the Abbe-refractometer of AR-200 model, and the boiling point was determined using the thermometer of 0-300⁰C capacity.

Automotive top coat was formulated in three stages: first the milling stage. This involved grinding and dispersion of 20.0 % (by weight) of rutile titanium dioxide pigment in 80 ml of

white spirit using 1000 ml ceramic mortar and pestle. The process of grinding was continued for 60 minutes; meanwhile testing of the fineness of incorporated pigment was measured using Hegman-gauge until getting size 1-5 micrometer (μm) fine particles following the standard of American Society of Testing Materials (ASTM- D- 817-96, 2010) for automotive top coats.

Table 1. Experiment design for formulation of the castor - seed-oil plasticized paint (CSOPP)

| Raw Materials | Percentage (by weight %) | Total weight (in gm) |
|----------------------|--------------------------|----------------------|
| Titanium dioxide | 20.00 | 200.00 |
| Castor seed oil | 24.00 | 240.00 |
| Xylene | 13.00 | 130.00 |
| White spirit | 6.00 | 60.00 |
| Cyclo-hexane | 4.00 | 40.00 |
| Trimethyl benzene | 4.00 | 40.00 |
| Alkyd resin | 24.00 | 240.00 |
| Methyl ethyl ketones | 2.00 | 20.00 |
| Nitrocellulose | 2.00 | 20.00 |
| Disperbyk | 1.00 | 10.00 |
| Total | 100.00 | 1000.00 |

Stabilization stage: Temperature of the dispersed pigment was maintained in the range of 26-27⁰C by addition of 80 ml xylene while stirring was continued to increase the intermolecular distance and prevent aggregation of the constituent-particles. 240 ml alkyd resin was added to the paint-blend and was stirred properly to ensure to get the good quality of paint.

Let down stage: it comprised the incorporation of other additives like cyclo-hexanes, nitrocellulose, plasticizer (castor- seeds oil) etc for getting improvement in property of paint such as the flexibility, brushability, plasticity to improve curing of the paint coatings. The temperature of the finished paints was allowed to drop from 72⁰C to 27⁰C before storing in an air-tight paint-pot.

Performance quality test: The specified quality tests were carried out on the paint samples and compared to the commercial automotive paint samples with respect to opacity, drying time, washability, specific gravity etc. The specific gravity test was carried out of the research samples according to ASTM/BIS standard. Opacity testing was performed by spreading the paint on readymade opacity-white-papers having black lines across them, and the hiding-capacity of the research paint was observed visually and found satisfactory.

The viscosity testing was done using a Ford-cup-B-4 viscometer at temperature 27-28⁰C with the help of a stop-watch to record the time for falling the last drop of the paint samples from cup's orifice. The paint sample was thinned down for further easy application before spraying on the mild steel-panels using a spray gun, while the storage

temperature was also determined to monitor the drying time [20, 21, 22].

III. RESULTS AND DISCUSSION

The castor-seed-oil was recovered by simple distillation method and the residual oil obtained was characterized with specified parameters. The results shown that the moisture content: $(0.30 \pm 0.01\%)$, specific gravity: (0.95 ± 0.02) , and refractive index @ 28°C : (1.79 ± 0.01) , flash point: $(256.00 \pm 1.20^{\circ}\text{C})$, viscosity @ 28°C : (0.425 ± 0.12) , pH: (5.80 ± 0.00) . The crude oil sample was characterized according to ASTM/BIS; they were lying within the range of acceptable industrial standard.

The attained yield as 48% makes the commercialization of the castor-seeds refer its feasibility and profitability. Also, the result of the investigation validates that the oil was to be of good quality and can be used for applications in food industry as food-additives and for other industrial purposes as well [4, 6, 20].

Table 2. The comparative values of the castor-seeds-oil sample to the commonly used drying oils on the basis of physical test

| Tests | Castor seed oil | Linseed oil | Cedar wood oil |
|--|----------------------------------|------------------------|-----------------------------|
| Appearance | Colorless to light yellow | Golden brown to yellow | Light yellow to dark yellow |
| Refractive Index @ 28°C | 1.79 ± 0.01 | 1.47 | 1.48 |
| Specific gravity (gm/cm^3) | 0.95 ± 0.02 | 0.91 | 0.92 |
| viscosity @ 28°C | 0.425 ± 0.12 | 0.80 | 0.97 |
| pH | 5.80 ± 0.00 | 5.1 | 5.4 |
| Boiling point ($^{\circ}\text{C}$) | 225 | 215 | 220 |
| Moisture content | $0.30 \pm 0.01\%$ | 0.40 | 0.42 |
| flash point | $256.00 \pm 1.2^{\circ}\text{C}$ | 245.00 | 250.00, |

Table 3: Results of quality control testes of paint samples

| Research Sample | Paint | Commercial Paint | |
|-----------------------------------|-----------------|-------------------|-----------------|
| Tests | Plasticizer | Unplasticized - 1 | Plasticized - 2 |
| Opacity | 100%, excellent | fair | better |
| Viscosity at 27°C | 91.00 | 95.00 | 97.00 |
| Specific | 1.13 | 1.66 | 1.16 |

| gravity (gm/cm^3) | | | |
|-------------------------------------|----|----|----|
| Drying time (in minutes): | | | |
| Dust-free time | 4 | 10 | 5 |
| Touch dry time | 10 | 20 | 15 |
| Tack free drying time | 10 | 20 | 15 |
| Hard dry time | 20 | 60 | 30 |

Above values of quality test of the research paint samples refer the superiority of formulated paint.

Table 4. Performance test observations of castor-seed-oil based coatings of micron sized pigments in different paint formulations

| Paint sample | Cross cut Adhesion Test | Gloss at 60° angle | Weathering test: QUV resistance test (in Hours) | Salt spray Test: (in hours) |
|-------------------|-------------------------|-----------------------------|---|-----------------------------|
| Formulated CSOP P | 100/100 (100%) | 98 | 600 hours passed | 648 Hours Passed |
| Commercial Paint1 | 99/100 (99%) | 95 | 552 hours | 600 hours |
| Commercial Paint2 | 100% | 96 | 576 hours | 624 hours |

The characterization of castor oil was carried out to assess its suitability in automotive paint formulation shown in table 2. The values of the refractive index of castor seed oil (1.79) and viscosity (0.425 at 28°C) are high as compared to the commercial linseed oil or cedar wood oil, which belong to the accepted industrial standard for auto-paint manufacturing [7,8, 20,21]. The high viscosity is an advantage to control the liquefying flow and rheology of automotive paints. The average specific gravity of ($0.95\text{gm}/\text{cm}^3$) of the castor-oil sample has been recognized for the proper dispersion stability of pigment particles alongwith compatibility for used solvents during the formulation process. The optimum percentage of titanium dioxide, castor seed oil and alkyd resin was kept as 20.00%, 24.00%, 24.00% by weight respectively, as shown in table-1, was determined in order to formulate a distinctive white glossy and plasticized automotive paint. The drying time of the castor oil based paint was monitored under the atmospheric condition and the period of film formation was recorded at 20-30 minutes, which was quite good for surface coatings according to Berger paint's standard (1998).

The opacity result of the castor seed oil plasticized auto-paint during testing indicated that the hiding ability is quite better than the unplasticized sample paint compared to the commercial paint [21, 28, 30]. This could be attributed to the cross-linking effect of the castor oil as plasticizer, when exposed to the atmospheric air along with oxygen [21, 35, 38]. The viscosity-value for plasticized paint sample was lower as shown on table 2, because of addition of the castor oil, reduces the cohesion of the intermolecular force along the chains and increases free flow, flexibility, elongation and workability of the paint components. It has been suggested that drying time of plasticized paints can generally be reduced due to the presence of the ricinoleic acid [21,30,37]. The stages of drying, from dust free time to touch dry, through tack dry and hard dry time, as shown on table 3, exhibited satisfactory results for the research plasticized automotive paint as compared with the unplasticized commercial paints. The castor seed oil plasticized automotive paint exhibited higher gloss, flexibility, increased adhesion, durability, smooth surface and provided additional protections to the substrate against corrosion and other weathering conditions, as observed on the coated steel panels[1,2,43,44,].

IV. CONCLUSIONS

On the basis of the analysis of the use of castor-seed-oil as a substitute of polymeric plasticizers in automotive paints can now robustly be recommended in order to minimize harmful solvent emission, to avoid the release of green house gases during paint formulations, applications and drying.

Incorporation of castor seed oil as plasticizers in surface coatings protect against corrosion, cracks, and improved attractive aesthetic looks. The result also refers that the oil can be classified as drying oil and plasticizer can be used extensively in the manufacturing of paint and vanishes. Considering the percentage yield of the castor seed oil which was 48%, introduced an alternative to the broadly used expensive, imported linseed oil in paint manufacturing sectors; castor seed oil may be established. The result of the investigation carried out on crude castor seed oil confirms the presence of ricinoleic acids, oleic acid, palmitic acid; an indication to good quality, that can be modified so as to be useful in chemical and paint industries as well.

V. ACKNOWLEDGEMENTS

The author is grateful to Prof. N.D. Pandey, Prof. S.S. Narvi, Prof. Parthasarthi Chakrabarti the Director of M.N.N.I.T. Allahabad, all the people of Corrosion Engg. Lab, I.I.T. Bombay, and R & D Lab, Berger Paints Limited, Kolkata for their help and encouragement during the research work.

REFERENCES

[1] X. Shi, Nguyen, T. A. Suo, Z. Liu, Y. Avci, R. "Surface and Coating Technology" 2009, 204, P: 237–245.

[2] Gan, S.N., Teo, K.T. "Paint Resin Technology", Vol. 28, no. 5, p. 283–292, 1999.

[3] E.P. Sabina, M.K. Rasod, L. Matthew, (2009), Studies on the protective effect of Ricinus Communis Leaves Extract on Carbon tetrachloride hepato-toxicity in Albino Rats, *Pharmacology* 2, 905-916.

[4] P. Kalaiselvi, B. Amuradha, C.S. Parameswari, (2003), Protective Effect of Ricinus Communis Leaf Extract against Paracetamol induced Oxidation of Unsaturated Lipids, *Hepato-toxicity, journal of*, (1-2), 97-105.

[5] M. Ghisari, Biomedicine, E.C. Benfield-Jorgensen (2009), Effect of Plasticizers and their mixtures on estrogens receptor and thyroid hormonal functions , *Journal of Toxicology*, 189(1), 67-77.

[6] N.J. Frank, (2005), *Alkyd Resins*, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VcH, Weinheim, 409.

[7] P. Slephannie, P. (2011), *Oldest Human Paint-making Studio Discovered in Caves*, *Live Science*, 14.

[8] F.C. David and J.H. Christopher (2000), *Plasticizers*, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VcH, Weinheim, 439.

[9] A.P. Needs, S.E. Caldwell, K.A. Mill, (1995), Mechanism of Free Radical Lipids, 30, 277-296.

[10] Sunyer, (2001), "Urban Air Pollution and Chronic Obstructive Pulmonary disease: a review" *European Respiratory journal*, 17(5), 1024-1033.

[11] Dole K.K., Keskar V. R., (1976)"Dehydration of castor oil", *Curr Sci.*, pp242-243

[12] Hamilton R. J., and Cast, J., (1999), Spectral properties of lipid.

[13] Ibiyemi S.O., Adepoju T.O., Okanlawon S.o., and Fadipe V.O.,(1992), "Emulsion preparation and stability, *journal of nutritional science*. 13,(1-2), 31-34.

[14] M. Daniel, (2007), Standard Specification of Linseed Oil for Paints, *Industrial Research and Standard Revision Acts*, section 20(25), S.I.159/1949.

[15] P. Oragwu Ifeoma, *Automotive Paint from Local Raw Material Castor Oil*, *AJER-ISSN 2320-0936*, Vol.02, issue-11, P: 272-275, 2013.

[16] G. Wollensak, E. Spoerl, T.Seiler, (2003), Riboflavin/ultraviolet induced collagen cross linking for the treatment of kartoconus, *American journal of Ophtalmol*, 135 (5), 620- 627.

[17] D.A. Morgan, (1971), Effect of Plasticizers on the Strength of a Plastic Motor Case, *Army Missile Research and Development*, 1, 23.

[18] D.S. Oguniyi (2006), Castor Oil; A Vital Industrial Raw Material, *Bioresource Technology*, 97(9), 1086- 1091.

[19] R.Victor, R.S. Jayalakshamma, (2005), Cost Effective, Qualitative Immersion Oil for Microscopy, *Anatomical Society of India*, 54(2), 7-12.

[20] J.A. Ibemesi and J.C. Attah (1990); Solvent Extraction of Oils of Rubber, Melon, Pumpkin and Oil Bean Seeds, *American Oil Chemist's Society*, 67(1), 25-27.

[21] American Society for Testing Materials (ASTM) International, (2010), *Chemical Analysis of Paints and Paint Materials*, D817-96, [102].

[22] ASTM, (1984). *American Standard of Testing Material (ASTM-D-1322, ASTM-D-93)*,

[23] Rial , Ghetie, Victor and Lauterbach, Brenda., (1999), "Selection of castor for divergent concentrations of ricin and ricinus communis Agglutinin and references therein" (PDF).*Crop science*, 39: 353-357.

[24] Wood M. (2001), "High-Tech castor plants May Open Door to domestic production" *Agricultural Research magazine* 49 (1).

[25] Galliano, F., Landolt, D., *Progress in Organic Coatings*, **2002**, 44, 217.

[26] Miskovic-Stankovic, V. B., Stanic, M. R., Drazic, D. M., *Prog. Org. Coat.*, **1999**, 36, 53.

- [27] Loos, C., Springer, G. S., Journal of Comp. Materials, **1979**, 13, 131.
- [28] Dietsche, F., Thomann, Y., Thomann, R., Mulhaupt, R., J. Appl. Polymer Science, **2000**, 75, 396.
- [29] Becker, O., Varley, R., Simon, G., Polymer, **2002**, 43(16) 4365.
- [30] Yang, L. H., Liu, F. C., Han, E. H., Prog. Org. Coatings., **2005**, 53, 91.
- [31] Umaka, S. V., Zheludkevich, M. L., Yasakau, K. A., Serra, R., Poznyak, S. K., Ferreira, M. G. S., Prog. Org. Coat., **2007**, 58, 127.
- [32] Xianming Shi, Tuan Ahn Nguyen, Zhiyong Suo, Yajun Liu, and Avic, R., Surface Coating Tech., **2009**, 204, 237.
- [33] Li, R., and Chen, L., A paint containing nano titanium oxide and nano silver, and its preparation method. CN 10027622, **2005**.
- [34] Yebra, D. M., Kiil, S., Johansen, K. D., Prog. Org. Coat., **2004**, 50, 75
- [35] Vasconcelos, M. T. S. D and Leal, M. F. C., Environ. Sci. Technol., **2001**, 35, 508.
- [36] Antonietta, Z. M., Stefania, Z., Rebecca, P., Riccardo, B. J., Inorg. Biochem. **1996**, 35, 291.
- [37] Stoimenov, P. K., Klinger, R. L., Marchin, G. L. and Klabunde, K. J., Langmuir **2002**, 18, 6679.
- [38] Yoichi, Y., Hiroshi, Y., Chikara, K. and Kei, I., Prog. Org. Coat. **2001**, 42, 150.
- [39] Shtykova, L., Fant, C., Handa, P., Prog. Organic Coatings, **2009**, 64.
- [40] Sakai, H., Kanda, T. and Shibata, H., Journal of American Chem. Soc. **2006**, 128, 4944.
- [41] White, S. R., Sottos, N. R., Geubelle, P. H., Nature, **2001**, 409, 794.
- [42] Cho, S. H., Andersson, H. M. and White, S. R., Adv. Mater. **2006**, 18, 99.
- [43] Shchukin, D. G., Lamaka, S. V. and Yasakau, K. A., J. Phys. Chem., **2008**, 112, 958.
- [44] Yuan Le, Pengtao Hou, Jiexin Wang and Jian-Feng Chen, Mater. Chem. Phys., **2010**, 120(2-3), 351-355.



Shambhu Sharan Kumar, Assistant Professor, Chemistry Dept., Birla Institute of Technology, Mesra, Off Campus, Allahabad- 211 010, India; M.Sc. Chemistry, M. Tech. (Surface Sc. & Engineering: N.I.T. Jamshedpur), Ph. D. (pursuing), M.I.Ch.E. (Life Member- Indian Institute of Chemical Engineers), M.I.S.T.E. (Life Member- Indian Society for Technical Education), M.I.A.Eng. (Member- International Association of Engineers, Hong Kong). His research area: synthesis of nano particles and their applications in high performance polymer nano composite coatings w.r.t. corrosion protection and weathering resistance.